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PREPARATION OF BIS[4-(3,4 DIMETHYLENE-PYRROLIDYL)-
PHENYL] METHANE AS A HIGH TEMPERATURE REACTIVE OLIGOMER

Raphael M. Ottenbrite, Joseph G. Smith and
Akira Yoshimatsu

Department of Chemistry
Virginia Commonwealth University
Richmond, Virginia 23284

INTRODUCTION

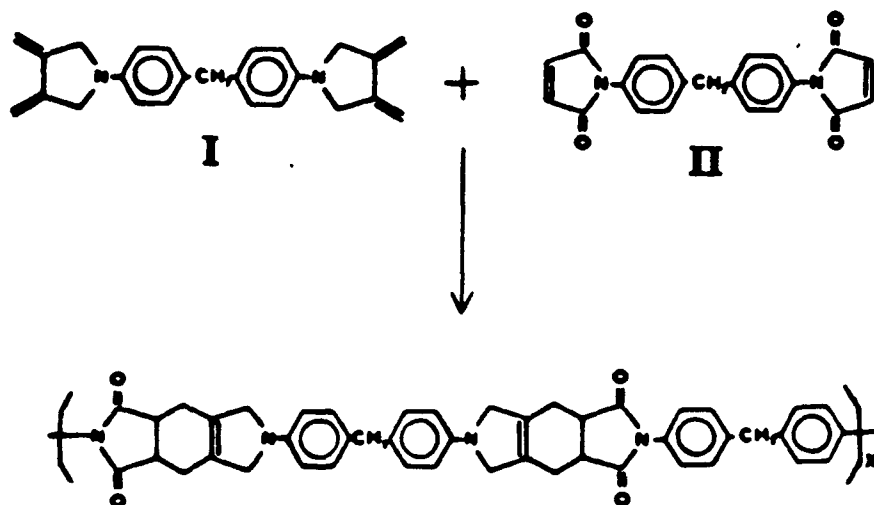
A major goal in the field of high temperature polymers has been to prepare aromatic polyimides that can be easily fabricated with the required thermal and physical properties for aerospace applications. Recent research has been directed to achieve polyimides that are:

- a) soluble in a common organic solvent
- b) melt-processable
- c) thermally curable without the evolution of volatile by-products(1)

The melt processability of polyimides can be enhanced by lowering the flow temperature using synthetic techniques such as the incorporation of aryl-ether and meta-phenylene linkages in the polymer backbone.

An approach by Harris (2), to obtain phenylated polyimides involves the Diels-Alder polymerization of phenylated biscyclopentadienones with bismaleimides. The problem with this process is that during the reaction, carbon monoxide is produced subsequent to the Diels-Alder addition. Furthermore, at temperatures of >300°C dehydrogenation, as well as other decomposition processes, occurs to yield a polymer with less solubility.

We have developed a unique monomer, N-phenyl-3,4-dimethylenepyrrolidine, that can be modified to form a bis(exocyclodiene) I for the preparation of polyimides by the Diels-Alder process (3). This bis(exocyclodiene) does undergo Diels-Alder reaction with bismaleimides II without the evolution of gaseous by-products. The objective of this research is to prepare high temperature polymeric materials by Diels-Alder polymerization that will maintain their integrity and toughness during long exposure time at elevated temperature.



EXPERIMENTAL

Synthesis of BIS[4-(3,4-Dimethylenepyrrolidyl)phenyl]-methane

The synthesis of phenyl methane was carried out by reacting 4,4'-methylenediamine arylenes with 2,3-bis-(bromomethyl)-1,3-butadiene. During the reaction, the flask was covered with foil to avoid light catalyzed polymerization of the diene group of the starting material and product. N_2 sweep appeared to help retard the oxidation of the product. The product, bis(3,4-dimethylenepyrrolidyl)arylene, was very reactive and readily undergoes self Diels-Alder addition. Since these dienes have poor solubility in organic solvents and poor stability, attempts to purify these monomers were not successful.

Self Diels-Alder Reaction of Bis[4-(3,4-dimethylenepyrrolidyl)phenyl] methane

Dimerization which can result from a Diels-Alder reaction between two exocyclic dienes was observed in the case of N-phenyl-3,4-dimethylenepyrrolidine. To evaluate the stability of these bisdiene compounds, bis[4-(3,4-dimethylenepyrrolidyl) phenyl] methane (5% monomer in $CDCl_3$) was heated at $50^\circ C$ and followed by 1H NMR spectroscopy. After heating at $50^\circ C$ for 7 h, new multiplet signals appeared at δ 2-3 region with decreasing endo protons of the exocyclic diene at δ 5.5 region. It is estimated that the reaction ratio by self Diels-Alder was 20-30% under model compound preparation conditions and 2-3% under conditions of polymerization based on the integration of the 1H NMR spectra.

Copolymerization of Bis[4-(3,4-dimethylenepyrrolidyl)-phenyl]methane with Bis[4-(Maleimidyl)phenyl]methane

A polymer powder was prepared from the prepolymer solution which contained equimolar amounts of bis[4-(3,4-dimethylenepyrrolidyl)-phenyl]methane I and bismaleimide II in solution. After standing overnight, the prepolymer solution became a gel. The polymer gel was washed with chloroform and acetone, and then dried in vacuo.

Polymer Film

Polymer films were prepared by casting the prepolymer solution onto a clean glass surface. The glass plates were held at room temperature overnight to allow the solvent to evaporate. The films were then heated at 120°C for 12 h to give transparent flexible polymer films. These films were heated another 12 h at 150°C.

RESULTS AND DISCUSSION

Copolymerization of Bis[4-(3,4-dimethylenepyrrolidyl]methane I with Bismaleimide II

It was observed that bis[4-(3,4-dimethylenepyrrolidyl)phenyl]methane reacts very rapidly with bismaleimide by Diels-Alder addition. However, this reaction is slower in acidic solvents, such as trifluoroacetic acid, due to the protonation of the nitrogen in the pyrrolidine ring. The polymerization of bis[4-(3,4-dimethylpyrrolidyl)methane with bismaleimide was followed by ¹H NMR spectroscopy. At 50°C in trifluoroacetic acid, complete polymerization could be achieved within 48 h. The polymerization yield was estimated to be 92% based on the integration of ¹H NMR spectrum.

The ¹H NMR peak height decreases for the bisdiene protons and the polymer backbone proton area increases during the reaction. The new methylene protons on the central ring due to the Diels-Alder addition, is consistent with the decreasing exocyclic diene peak. Consequently, it is considered that the Diels-Alder reaction is the predominant process in this polymerization. The inherent viscosity determined during the polymerization was plotted against the ¹H NMR signal height due to the newly formed methylene protons (Figure 1). It appears

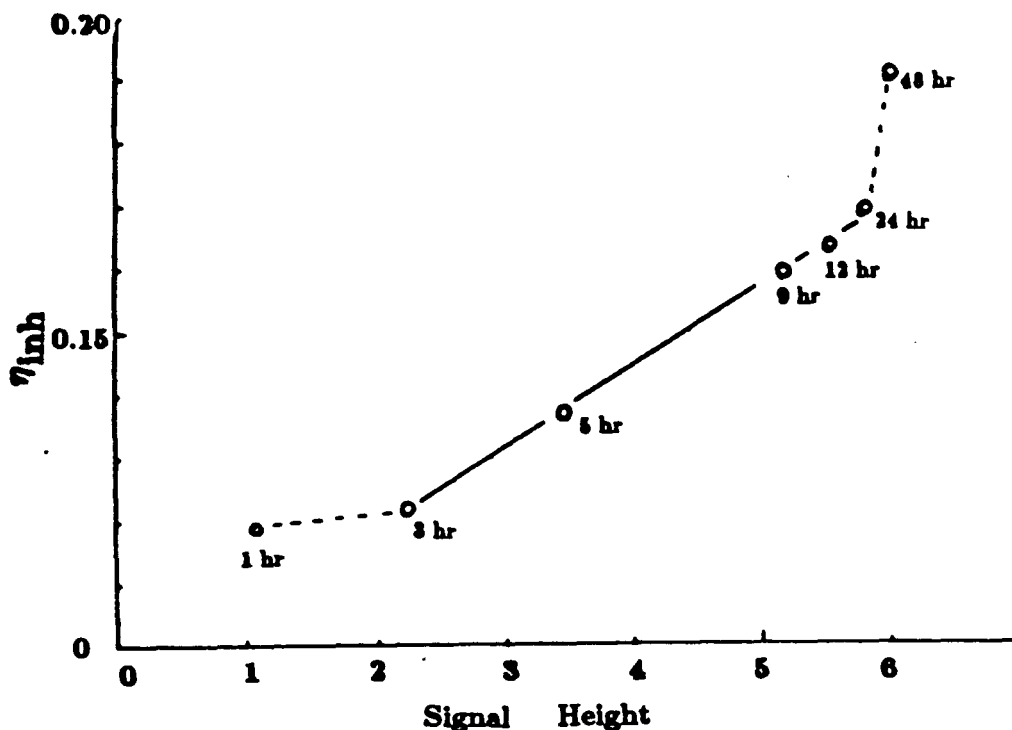


Figure 1: Relationship of viscosity to methylene proton NMR height during reaction.

that, after formation of oligomer dimers and trimers within the first 3 h, the elongation of the polymer chain takes place as indicated by the increasing viscosity with time.

The Effect of Mole Ratio of Monomer on Film Properties

After determining the monomer concentration of bis[4-(3,4-dimethylenepyrrolidyl)phenyl]methane concentration by ^1H NMR spectrum, the bismaleimide comonomer was added to the solution to make the prepolymer solution. The polymer films were then prepared from this prepolymer solution. Shown in Table I are the film properties which were found to depend on the mole ratio of both monomers. The addition of 20-30% less bismaleimide II than bisdiene I made good flexible films. This observation might be explained by the fact that the 20-30% of the bisdiene may be undergoing a self Diels-Alder process that was described earlier.

Table 1: The Effect of Mole Ratio of Monomers on Film Properties			
Mole Ratio (I) (II)		Solution Viscosity	Film Property
1.0	1.0	nonviscous	brittle
1.0	0.9	nonviscous	brittle
1.0	0.8	viscous -> gel	flexible
1.0	0.7	viscous -> gel	flexible
1.0	0.6	nonviscous	brittle

Solubility

The original polymer film was insoluble in organic solvents. Hot concentrated sulfuric acid was used as a solvent for five different polymer films which had different curing temperatures after casting (Table 2). The polymer films that were treated at temperatures above 120°C were not soluble in hot H_2SO_4 . This decreased solubility may be due to a crosslinking reaction taking place in the polymer film after heating at high temperatures and/or oxidation of the pyrrolidine ring to the aromatic pyrrole.

Table 2: Solubility of the Polymer Film in Concentrated H_2SO_4	
Curing Temperature (°C)	Solubility
25	P
50	P
120	i
160	i
200	i

Thermal Analysis

The thermal stability and decomposition temperature of the polymer films were analyzed by TGA. The measurements were carried out in N₂ and air atmosphere, respectively. The polymer film was thermally stable with only 10% weight loss at 357°C and 20% weight loss occurred at 413°C in nitrogen. The thermal data of the polymer film are tabulated in Table 3. On the other hand, TGA plots in air showed different behavior. There two plateau regions in the TGA curve were observed. The second rapid weight loss occurred above 400°C and was indicative of total decomposition of the polymer backbone. The first moderate weight loss occurred at much lower temperatures (239°C).

Table 3: Thermal Properties of Polymer Film		
Atmosphere	T (°C) 10% wt. loss	T (°C) 20% wt. loss
nitrogen	357	413
air	239	385

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